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13. ABSTRACT (Maximum 200 words)

This project explored the potential as photochromic substrates for optical memory systems of transition metal complexes in which two d^1 transition metal centers are spin paired through a linear oxo bridge. The project was based on the discovery of a dinuclear W(V) tungstenocene derivative in which irradiation into the strong visible region absorbance associated with the d^1-d^1 oxo bridged chromophore led to marked photochromism following photodisproportionation to a 1:1 mixture of d^0 and d^2 complexes. Examination of the large class of d^1-d^1 oxo bridged dimers containing $[M^V_2O_3]^{4+}$ ($M = Mo, W$) cores stabilized by bis-chelate dithiocarboxylate-type ligands $[S_2EX_n]^-$ led to the observation that dibenzylidithiocarbamates complexes of these cores undergo an analogous thermally reversible photochromic disproportionation, but dithiophosphate complexes undergo irreversible wavelength dependent photo-bleaching; the complexes are not themselves photoactive but are destroyed through photolysis of d^0 products of thermal disproportionation products. Both dithiocarbamate and xanthate complexes of the $[Mo^V_2O_3]^{4+}$ core are fluxional, participating in a process in which there is rapid intramolecular exchange of bridging and terminal oxo groups.

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FINAL REPORT

**Optical Memory Systems Based on Transition Metal
Photochromism: Photodisproportionation of d^1 - d^1 Dimers with
Linear Oxo Bridges**

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Submitted February 17, 1997

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Objective and Approach

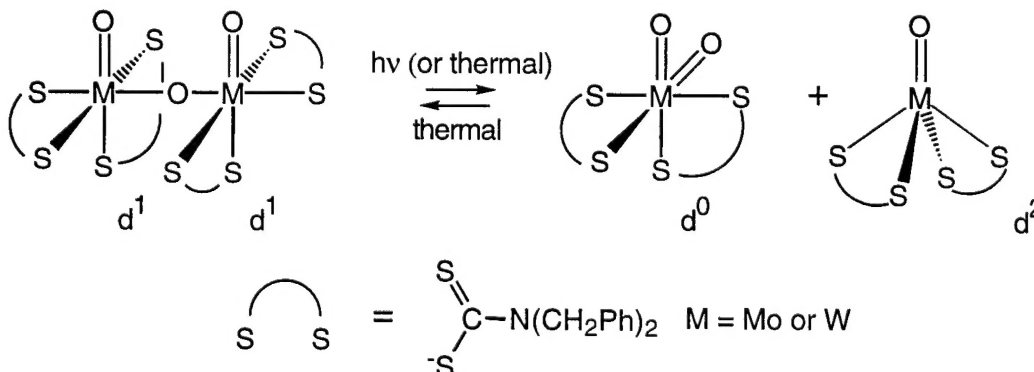
The objective of this project was to explore the potential of transition metal complexes in which two d^1 centers are spin paired through a linear oxo bridge as photochromic substrates for optical memory systems. Such complexes are characteristically intensely colored, and the project was based on our discovery of an unprecedented reaction in which one such complex ($[W(\eta^5-C_5H_5)_2(CH_3)_2(\mu-O)]^{2+}$) exhibited marked photochromism following irradiation (in acetonitrile solution) into the strong visible region absorbance associated with the d^1-d^1 oxo bridged chromophore. The photo reaction responsible for the color change involves photodisproportionation to give a W(VI) terminal oxo complex together with a solvent trapped W(IV) complex, and our initial approach had two principal objectives:

- To evaluate the technological potential of the photochromic behavior of $[W(\eta^5-C_5H_5)_2(CH_3)_2(\mu-O)]^{2+}$ by characterizing the photochemical processes underlying the behavior, particularly whether the disproportionation was promoted by irradiation into other absorbances in addition to the visible band associated with the bridging oxo chromophore; wave length specific behavior would greatly increase the potential of these materials as substrates for an optical memory system.
- To examine the photochemistry of other d^1-d^1 oxo bridged dimers, particularly those known to undergo thermal reductive disproportionation, to determine the generality of photo induced disproportionation in these systems; access to a range of photodisproportionation substrates would increase the likelihood of discovering a system with the characteristics required for an optical memory substrate.

Results and Conclusions

Our first achievement under the initial phases of our ONR sponsored research was to establish that the photo-disproportionation of d^1-d^1 dimers with linear oxo bridges is not unique to $[W(\eta^5-C_5H_5)_2(CH_3)_2(\mu-O)]^{2+}$. This emerged from a study of the dibenzylthiocarbamato complexes $[(WO\{S_2CN(CH_2Ph)_2\}_2)_2(\mu-O)]$ and $[(MoO\{S_2CN(CH_2Ph)_2\}_2)_2(\mu-O)]$, which are representative examples of the well known class of molecules in which a linear oxo bridge spin pairs two d^1 W(V) or Mo(V) centers within a $[M^V_2O_3]^{4+}$ core containing two mutually syn or anti terminal oxo ligands perpendicular to the M-O-M axis. It had been known for some time that many $[Mo_2O_3]^{4+}$ complexes are in thermal equilibrium with the corresponding Mo(IV) and Mo(VI) disproportionation products, and what we established was that this equilibrium could be accessed photochemically as well as thermally as shown in Scheme 1.

Scheme 1



The thermal equilibrium lies well on the side of dimer formation, and photodisproportionation results in marked photochromism. Thermal recombination is rapid at room temperature, making it experimentally difficult to determine parameters such as quantum yields and the action spectrum, but our results establish that the failure of earlier workers to recognize the existence of the photodisproportionation reaction led to inaccurate reports of the optical properties of these systems, including errors in parameters as basic as the extinction coefficients.

Our discovery of the photodisproportionation reaction of dithiocarbamate complexes of d^1-d^1 oxo bridged dimers has been published as: **Evidence for Photodisproportionation of d^1-d^1 Dimers $[(MO\{S_2CN(CH_2Ph)_2\}_2)_2O]$ ($M = Mo, W$) Containing Linear Oxo Bridges and for Oxygen Atom Transfer from $[WO_2\{S_2CN(CH_2Ph)_2\}_2]$ to PEt_3 .** S. Lee, D. L. Staley, A. L. Rheingold, and N. John Cooper, *Inorg. Chem.*, 1990 29, 4391.

The obvious working hypothesis at this stage was that photodisproportionation would be a general reaction of d^1-d^1 dimers spin paired through a linear oxo bridge, and we began to test this by surveying the reactivity of other members of the group of compounds in which an $[MoV_2O_3]^{4+}$ core is complexed by four bis-chelate dithiocarboxylate-type ligands to give a $[MoV_2O_3(S_2EX_n)_4]$ complex. We turned first to examples in which the $[S_2EX_n]^-$ ligands were dithiophosphates, as in $[MoV_2O_3\{S_2P(OEt)_2\}_4]$, $[MoV_2O_3\{S_2P(OPh)_2\}_4]$, and $[MoV_2O_3\{S_2P(OMe)_2\}_4]$, and established that all three of these dithiophosphate complexes are indeed photosensitive. Their photochemical behavior differs, however, from that of the dithiocarbamate complexes in that photolysis in acetonitrile causes *irreversible* bleaching rather than true photochromism. We initially assumed that this indicated irreversible trapping of coordinatively unsaturated d^2 disproportionation products $[Mo^{IV}O\{S_2P(OR)_2\}_2]$ by the polar solvent, but similar behavior is observed in toluene and a more detailed examination established that the reaction involves more subtle and intriguing effects than a simple change in the kinetics or thermodynamics of a follow-up trapping reaction.

What we discovered is that solutions of the dithiophosphate complexes are *not* sensitive to irradiation into the main visible absorptions at 500 nm, but *are* decomposed by irradiation at wavelengths below 400 nm. Disappearance quantum yield studies have quantified this dramatic wavelength dependence, and have established $\Phi_{310}:\Phi_{510}$ ratios of >150 , >180 and >60 respectively for the Et, Ph and Me cases. These values are too large to be readily rationalized in terms of the intrinsic photophysical properties of the Mo(V) dimers, and we have proposed that the dimers are not themselves photoactive but are destroyed through photolysis of the d^0 disproportionation products $[MoO_2\{S_2P(OR)_2\}_2]$ as generated in a thermal disproportionation equilibrium. This suggestion is supported by ^{31}P NMR quantification of the disproportionation equilibria for all three complexes, and the photodecomposition mechanism has been confirmed in the case where $R = Et$ by the independent determination that the d^2 disproportionation product $[MoO\{S_2P(OEt)_2\}_2]$ is photostable while the d^0 complex $[MoO_2\{S_2P(OEt)_2\}_2]$ is photosensitive. $[MoO_2\{S_2P(OEt)_2\}_2]$ has a disappearance quantum yield at 310 nm of 0.12, but is unaffected by visible light because it does not absorb in the visible. This observation was a disappointment in terms of the generality of photodisproportionation in d^1-d^1 oxo bridged dimers, but did establish the intriguing idea that a thermal pre-equilibrium could be used to give a photochromic reaction dramatic wavelength dependence.

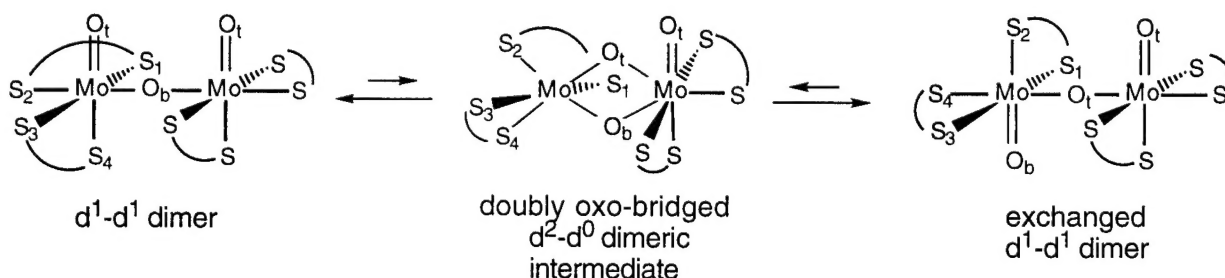
Our observation of wavelength dependent photolysis of dithiophosphate complexes of Mo(V) has been published as: **Marked Wavelength Dependence in Photolyses of Dithiophosphate Complexes of the $[MoV_2O_3]^{4+}$ Core through a Photoactive Intermediate Accessed by a Secondary Thermal Equilibrium.** R. L. Thompson, S. J. Geib and N. J. Cooper, *Inorg. Chem.*, 1993, 32, 6076.

When we began our ONR sponsored studies of the photochemistry of d^1-d^1 oxo bridged dimers containing $[MoV_2O_3]^{4+}$ cores we had an understanding of the structural chemistry of

complexes of this core with bis-chelate dithiocarboxylate ligands which we believed would provide an adequate background for any solution or polymer matrix studies of the photochemistry of these systems which we wished to undertake. Thus we knew that the complexes often participated in thermal disproportionation equilibria involving Mo(IV) and Mo(VI) disproportionation products of the $[\text{Mo}^{\text{IV}}\text{O}(\text{S}_2\text{EX}_n)_2]$ and $[\text{Mo}^{\text{VI}}\text{O}_2(\text{S}_2\text{EX}_n)_2]$ types, and that the dimers could exist as syn or anti isomers, but we assumed that the dimers were rigid with respect to intramolecular rearrangements. What we discovered, however, is that the assumption of rigid dimer cores is completely untrue, at least in cases which the $[\text{Mo}^{\text{V}}_2\text{O}_3]^{4+}$ core is complexed by dithiocarbamate or xanthate ligands. Thus the dithiocarbamate complex $[\text{Mo}_2\text{O}_3\{\text{S}_2^{13}\text{CN}(\text{CH}_2\text{Ph})_2\}_4]$ and the xanthate complexes $[\text{Mo}_2\text{O}_3(\text{S}_2^{13}\text{COEt})_4]$ and $[\text{Mo}_2\text{O}_3(\text{S}_2^{13}\text{CO}^i\text{Pr})_4]$ are fluxional on the NMR time scale, participating in a process in which thiocarboxylate ligands which have sulfur trans to the bridging oxo group are exchanged with thiocarboxylate ligands which have sulfur trans to a terminal oxo group.

The most reasonable interpretation of the fluxionality of all three molecules is that it involves exchange of binding and terminal oxo groups within the molecules, and we have proposed (Scheme 2) that this involves a transition state in which the linear oxo bridge has been replaced by two bent oxo bridges. The activation parameters for exchange in all three molecules are very similar, consistent with a common mechanism, and in all three cases there is only a small entropic contribution to the free energy barrier to exchange. This argues strongly against a dissociative mechanism for exchange and supports the proposal in Scheme 2.

Scheme 2



The importance of this result for the development of an optical memory medium based on the $[\text{Mo}_2\text{O}_3]^{4+}$ chromophore is that any such medium would obviously consist of a dispersion or solution of a $[\text{Mo}_2\text{O}_3]^{4+}$ complex within a polymer (or glass) matrix, and if such complexes are flexible rather than rigid, as implied by these results, they are much more likely to be able to undergo photochemical reactions within a polymer matrix which are similar to those which they undergo in solution.

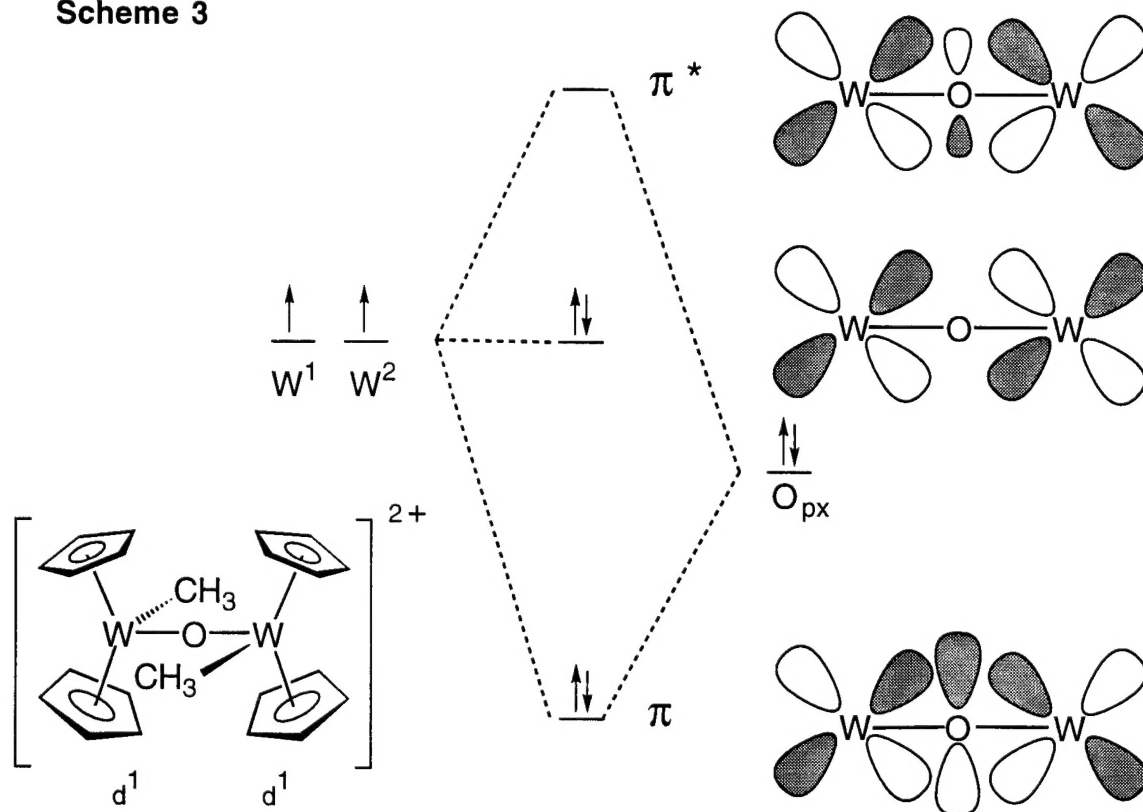
Our observation of fluxionality in $[\text{Mo}^{\text{V}}_2\text{O}_3]^{4+}$ cores has been published as: **Intramolecular Bridge/Terminal Oxo Exchange within $[\text{Mo}^{\text{V}}_2\text{O}_3]^{4+}$ Complexes Containing Linear Oxo Bridges**, R. L. Thompson, S. Lee, S. J. Geib and N. John Cooper, *Inorg. Chem.*, 1993, 32, 6067.

As we have expanded our knowledge of photodisproportionation and other photochemical reactions of $\text{d}^1\text{-d}^1$ oxo bridged dimers we have come to appreciate that photodisproportionation of $[\{\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)\}_2(\mu\text{-O})]^{2+}$ is unique in that: 1) the reaction occurs under conditions under which thermal disproportionation is slow; 2) the reaction is irreversible because the d^2 product is trapped by the acetonitrile solvent. This dimer is thus an ideal substrate with which to compare photochemical and thermal disproportionation of a $\text{d}^1\text{-d}^1$ oxo bridged dimer since the two processes can be studied independently, and we therefore undertook a kinetic and quantum yield study of disproportionation of $[\{\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)\}_2(\mu\text{-O})]^{2+}$ in which we established that thermal disproportionation has a large enthalpic barrier of $\Delta H^\ddagger = 33.7 \pm 1.7$ kcal mole⁻¹ but is entropically

avored, as would be anticipated for a dissociative reaction, with $\Delta S^\ddagger = 25.1 \pm 5.2 \text{ cal K}^{-1} \text{ mole}^{-1}$. More importantly, we have established that both the UV and visible absorptions of the dication are photoactive with respect to disproportionation with quantum yields of 0.081 in the UV at 310 nm and 0.014 in the visible at 530 nm.

These quantum yields are mechanistically intriguing. We have proposed, consistent with earlier studies, that the strong visible absorptions at ca 500 nm which are a common characteristic of d^1 - d^1 complexes spin paired through a linear oxo bridge arise from a HOMO-LUMO transition which is unusually low in energy because of the small gap between the non-bonding middle orbital and the anti-bonding upper orbital in the 3-center, 4-electron π -interaction between the two d^1 metal centers and the bridging oxygen (as illustrated for this case in Scheme 3), and has considerable intensity as a consequence of the MLCT component of such an absorption.

Scheme 3



Since this excitation corresponds to population of an anti-bonding orbital we had speculated that it might be dissociative, and that population of the corresponding excited state might be a required step in the photodisproportionation reaction. The quantum yield data, however, argue strongly against this—the lowest excited state may or may not be dissociative, but the markedly higher quantum yield for dissociation in the UV ($\Phi_{310}:\Phi_{530} = 5.8$) implies that this is not the principal excited state from which the dissociation is accessed, since the lower excited state should not be more efficiently accessed from a higher state than it is by direct excitation.

Our study of thermal and photochemical disproportionation in the tungstenocene dimer has been published as: **Thermal and Photochemical Disproportionation of the Oxo-Bridged Dimer** $[\{W^V(\eta^5-C_5H_5)_2(CH_3)\}_2(\mu-O)][PF_6]_2$. R. L. Thompson, M. D. Hopkins, N. J. Cooper, and S. Lee, *Organometallics* 1995, 14, 1969.

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Highlighted Presentation

On August 24, 1992 I presented our discovery that dithiophosphate complexes of the $[\text{MoV}_2\text{O}_3]^{4+}$ core undergo photobleaching in a reaction which exhibits marked wavelength dependence because the bleaching results from photolysis of a d^0 monomer of the type $[\text{MoO}_2\{\text{S}_2\text{P}(\text{OR})_2\}_2]$ (present as a component of the thermal disproportionation equilibrium between the Mo^{V} dimer and the corresponding Mo^{VI} and Mo^{IV} monomers) at the 204th ACS National Meeting in Washington DC. The material covered corresponded to that in publication number 3 below. The presentation was well attended, and provoked a lively question and answer session.

Publications supported by ONR grant N00014-90-J-1762

A. Book Chapters:

none

B. Published papers in refereed journals:

- (1) Evidence for Photodisproportionation of d^1 - d^1 Dimers $[(\text{MO}\{\text{S}_2\text{CN}(\text{CH}_2\text{Ph})_2\}_2)_2\text{O}]$ ($\text{M} = \text{Mo}, \text{W}$) Containing Linear Oxo Bridges and for Oxygen Atom Transfer from $[\text{WO}_2\{\text{S}_2\text{CN}(\text{CH}_2\text{Ph})_2\}_2]$ to PET_3 . S. Lee, D. L. Staley, A. L. Rheingold, and N. John Cooper, Inorg. Chem., 1990 29, 4391.
- (2) Intramolecular Bridge/Terminal Oxo Exchange within $[\text{MoV}_2\text{O}_3]^{4+}$ Complexes Containing Linear Oxo Bridges, R. L. Thompson, S. Lee, S. J. Geib and N. John Cooper, Inorg. Chem., 1993, 32, 6067.
- (3) Marked Wavelength Dependence in Photolyses of Dithiophosphate Complexes of the $[\text{MoV}_2\text{O}_3]^{4+}$ Core through a Photoactive Intermediate Accessed by a Secondary Thermal Equilibrium. R. L. Thompson, S. J. Geib and N. J. Cooper, Inorg. Chem., 1993, 32, 6076.
- (4) Thermal and Photochemical Disproportionation of the Oxo-Bridged Dimer $[\{\text{W}^{\text{V}}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)_2(\mu\text{-O})\}][\text{PF}_6]_2$. R. L. Thompson, M. D. Hopkins, N. J. Cooper, and S. Lee, Organometallics 1995, 14, 1969.

- (5) Oxo Complexes of Tungstenocene via Oxidation of $[W(\eta^5-C_5H_5)_2(OCH_3)(CH_3)]$ and Related Reactions: Synthesis, Structural Characterization, and Photodisproportionation of the Spin Paired d^1-d^1 Oxo Bridged Dimer $[\{ W(\eta^5-C_5H_5)_2(CH_3) \}_2(\mu-O)]^{2+}$ and Synthesis and Characterization of the d^0 Terminal Oxo Complex $[W(\eta^5-C_5H_5)_2(CH_3)(O)]^+$. P. Jernakoff, J. R. Fox, J. C. Hayes, S. Lee, B. M. Foxman and N. J. Cooper, *Organometallics* 1995, **14**, 4493.

Technical Reports supported by ONR grant N00014-90-J-1762

Technical Report No 1, submitted 6-19-91:

Evidence for Photodisproportionation of d^1-d^1 Dimers $[(MO\{S_2CN(CH_2Ph)_2\}_2)_2O]$ ($M = Mo, W$) Containing Linear Oxo Bridges and for Oxygen Atom Transfer from $[WO_2\{S_2CN(CH_2Ph)_2\}_2]$ to PEt_3 . S. Lee, D. L. Staley, A. L. Rheingold, and N. John Cooper.

Technical Report No 2, submitted 2-15-93:

Oxo Complexes of Tungstenocene via Oxidation of $[W(\eta^5-C_5H_5)_2(OCH_3)(CH_3)]$ and Related Reactions: Synthesis, Structural Characterization, and Photodisproportionation of the Spin Paired d^1-d^1 Oxo Bridged Dimer $[\{ W(\eta^5-C_5H_5)_2(CH_3) \}_2(\mu-O)]^{2+}$ and Synthesis and Characterization of the d^0 Terminal Oxo Complex $[W(\eta^5-C_5H_5)_2(CH_3)(O)]^+$. P. Jernakoff, J. R. Fox, J. C. Hayes, S. Lee, and N. J. Cooper.

Technical Report No 3, submitted 2-15-93:

Marked Wavelength Dependence in Photolyses of Dithiophosphate Complexes of the $[Mo^V_2O_3]^{4+}$ Core through a Photoactive Intermediate Accessed by a Secondary Thermal Equilibrium. R. L. Thompson, S. J. Geib and N. J. Cooper.

Technical Report No 4, submitted 2-15-93:

Intramolecular Bridge/Terminal Oxo Exchange within $[Mo^V_2O_3]^{4+}$ Complexes Containing Linear Oxo Bridges, R. L. Thompson, S. Lee, S. J. Geib and N. John Cooper.

Technical Report No 5, submitted 7-31-89:

The Thermal and Photochemical Disproportionation of the Oxo-Bridged Dimer $[\{ W^V(\eta^5-C_5H_5)_2(CH_3) \}_2(\mu-O)] [PF_6]_2$. R. L. Thompson, S. Lee, M. D. Hopkins, and N. J. Cooper.